

1 Attorney Docket No. 83346

2
3 MOLYBDENUM-COPPER COMPOSITE MATERIAL
4

5 STATEMENT OF GOVERNMENT INTEREST

6 The invention described herein may be manufactured and used
7 by or for the Government of the United States of America for
8 governmental purposes without the payment of any royalties
9 thereon or therefore.
10

11 CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

12 This patent application is co-pending with one related
13 patent application entitled STAINLESS STEEL-COPPER COMPOSITE
14 MATERIAL (Attorney Docket No. 83344), by the same inventor as
15 this application.
16

17 BACKGROUND OF THE INVENTION

18 (1) Field of the Invention

19 The present invention relates to a molybdenum-copper
20 composite material which may be used to manufacture parts and
21 tools requiring working temperatures up to 1,000 degrees
22 Centigrade and to a method of making the composite material to a
23 desired form using either cold pressing or selective laser
24 sintering.

1 (2) Description of the Prior Art

2 Sintered copper alloys are known in the art. For example,
3 U.S. Patent No. 4,935,056 to Miyasaka illustrates a wear-
4 resistant copper-base sintered oil containing bearing material
5 having a structure which contains 2 to 11% by weight of tin and
6 1 to 20% by weight of cobalt and further includes 2 to 15% by
7 weight of at least one of molybdenum disulfide, graphite and
8 lead serving as solid lubricants. Dispersed throughout the
9 structure is cobalt at an average particle size equal to or less
10 than 20 microns.

11 U.S. Patent No. 5,824,922 to Aonuma illustrates a wear-
12 resistant sintered alloy having a general composition consisting
13 essentially of in weight ratio 0.736 to 9.65% nickel, 0.736 to
14 2.895% copper, 0.294 to 0.965% molybdenum, 0.12 to 6.25%
15 chromium, and 0.508 to 2.0% carbon with the balance being iron,
16 and inevitable impurities. The alloy has a metallic structure
17 in which there are dispersed (1) a martensite, (2) a bainite
18 having a nucleus of sorbite and/or upper bainite surrounding
19 said nucleus, (3) an austenite having a high nickel
20 concentration, and (4) a hard phase surrounding with a ferrite
21 having a high chromium concentration and composed mainly of a
22 chromium carbide.

23 U.S. Patent No. 5,870,663 to Stucker et al. illustrates a
24 wear-resistant Zirconium-DiBoride (ZrB_2)-Copper Alloy composite

1 electrode. Wherein the first furnace cycle produces a sintered
2 shaped form which is about 30 vol.% to about 70 vol.% occupied
3 by sintered ZrB_2 . Wherein the first furnace cycle comprises
4 heating the desired form room temperature to about 1,300 degrees
5 C to about 1,900 degrees C. Wherein the sintered ZrB_2 is then
6 contacted with a copper alloy comprised of up to about 3 wt.%
7 boron and up to about 10 wt.% nickel. Wherein a second furnace
8 cycles is used to heat the sintered ZrB_2 and copper alloy above
9 the melting point of the copper alloy to infiltrate the ZrB_2 with
10 copper alloy to form a ZrB_2 /copper alloy composite electrode.

11 Despite the existence of these materials, there exists a
12 need for a material that offers the ability to create tools and
13 prototype parts requiring working temperatures up to 1000
14 degrees Centigrade.

15

16 SUMMARY OF THE INVENTION

17 Accordingly, it is an object of the present invention to
18 provide a composite material that offers the ability to create
19 tools and prototype parts requiring working temperatures up to
20 1000 degrees Centigrade.

21 It is a further object of the present invention to provide
22 a composite material as above which has a low coefficient of
23 thermal expansion.

1 It is still a further object of the present invention to
2 provide a method for manufacturing the above composite material.

3 The foregoing objects are attained by the composite
4 material and method of the present invention.

5 In accordance with the present invention, a composite
6 material is provided which has a molybdenum particulate and an
7 oxygen free copper matrix. The molybdenum is preferably present
8 in an amount of 35 - 65 vol% with the balance being of oxygen
9 free copper.

10 Also, in accordance with the present invention, a method
11 for manufacturing a molybdenum-copper composite material broadly
12 comprises forming a mixture of molybdenum, phenolic, and wax,
13 forming the mixture into a green form using either a selective
14 laser sintering process or a cold pressing process, placing the
15 green form and oxygen free copper into the furnace adjacent to
16 the green form, and subjecting the green form and the oxygen
17 free copper to a furnace cycle. During the furnace cycle the
18 wax and phenolic thermoset resin is vaporized and the molybdenum
19 is sintered. Additionally, the sintered molybdenum substrate,
20 which is contacted with copper, is heated above the melting
21 point of the copper which causes the copper to infiltrate the
22 molybdenum substrate, forming the molybdenum-copper composite
23 part.

1 Other details of the molybdenum-copper composite material,
2 as well as other objects and advantages attendant thereto, are
3 set forth in the following detailed description.

4
5 DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

6 The molybdenum-copper composite material is a particulate
7 composite created from molybdenum, phenolic, wax, and oxygen
8 free copper. The material is manufactured using an indirect
9 selective laser sintering (SLS) process, where a
10 molybdenum/phenolic/wax powder mixture is initially sintered
11 into a green form. Upon completion of sintering, the green form
12 is placed through a furnace cycle for de-binding and
13 infiltration of the oxygen free copper.

14 Molybdenum is a hard, malleable, ductile, high melting,
15 silver white metal with a body-centered cubic crystalline
16 structure. It is a metallic element which is most frequently
17 used as an alloying addition in alloy and stainless steels. Its
18 alloying versatility is unmatched because its addition enhances
19 strength, hardenability, weldability, toughness, elevated
20 temperature strength and corrosion resistance. Alloys
21 containing molybdenum are used in making high-speed cutting
22 tools, aircraft parts, and forged automobile parts. Because it
23 retains its strength and structure at very high temperatures, it
24 has found use in certain critical rocket and missile parts.

1 Molybdenum is not attacked by air at ordinary temperature, but
2 at elevated temperatures, it oxidizes to form molybdenum oxide.
3 Molybdenum melts at about 2617 degrees Centigrade.

4 The desired material properties of molybdenum is as
5 follows:

Property	Molybdenum
Density (g/cm ³)	10.22
Tensile Yield Strength (MPa)	550
Ultimate Tensile Strength (MPa)	650
Modulus of Elasticity (GPa)	324.8
Hardness (Vickers, Gpa)	200
Coefficient of Thermal Expansion (m/m/°C)	5.04E-6
Thermal Conductivity (W/mK)	146
Melting point (°C)	2,614

6
7 Phenolic is a thermoset synthetic resin generally employed
8 as a molding material for the making of mechanical and
9 electrical parts. There are hundreds of different phenolic
10 molding compounds and in general they have a balance of
11 moderately good mechanical and electrical properties and are
12 generally suitable in temperatures up to 160 degrees Centigrade.
13 The resins are marketed usually in a granular form, partly
14 polymerized for molding under heat and pressure which completes
15 the polymerization process, making the product infusible and
16 relatively insoluble.

1 The desired material properties of the phenolic thermoset
2 resin is as follows:

Property	Phenolic
Density (g/cm ³)	1.1 - 1.3
Tensile Yield Strength (MPa)	52.0
Ultimate Tensile Strength (MPa)	60.0
Ultimate Compressive Strength (MPa)	140.0
Modulus of Elasticity (GPa)	6.0
Hardness	130.0, Rockwell M
Coefficient of Thermal Expansion (m/m/°C)	77.0E-6
Thermal Conductivity (W/mK)	0.2
Electrical Resistivity (Ohm-cm)	5.0E11
Melting point (°C)	---
Maximum Service Temperature (°C)	160

3
4 Oxygen-free high conductivity copper (C10100) is produced
5 by the direct conversion of selected refined cathodes and
6 castings under carefully controlled conditions to prevent any
7 contamination of the pure oxygen-free metal during processing.
8 The method of producing oxygen-free high conductivity copper
9 insures extra high grade of metal with a copper content of 99.9%
10 by weight. With so small a content of extraneous elements, the
11 inherent properties of elemental copper are brought forth to a
12 high degree. Characteristics are high ductility, high
13 electrical and thermal conductivity, high impact strength, good
14 creep resistance, ease of welding, and low volatility under high

vacuum. Some typical uses for copper alloy C10100 in the electrical and electronic industries are bus bars, bus conductors, wave guides, hollow conductors, lead-in wires and anodes for vacuum tubes, glass to metal seals and others.

The desired material properties of the oxygen free copper is as follows:

Property	O ₂ Free Cu
Density (g/cm ³)	8.96
Tensile Yield Strength (MPa)	33.3
Ultimate Tensile Strength (MPa)	210
Modulus of Elasticity (GPa)	110
Hardness (Vickers, Gpa)	49
Coefficient of Thermal Expansion (m/m/°C)	17.64E-6
Thermal Conductivity (W/mK)	346
Melting point (°C)	1,083

To form the composite material of the present invention, a mixture of molybdenum, phenolic, and wax is formed. The mixture may be shaped into the form of a part or component to be produced. The mixing of molybdenum particles with wax and phenolic thermoset resin particles should be done in a way such that the particles are evenly dispersed. The preferred molybdenum, wax, and phenolic thermoset resin particle size for the selective laser sintering shaping method should be between 10 microns and 145 microns, with an average particle size of between 20 microns and 45 microns. This is because the powder

1 in the selective laser sintering machine is moved by a counter-
2 rotating roller, and this method of powder transfer does not
3 work well for finer powders.

4 In mixing the particles, the recommended molybdenum, wax,
5 and phenolic thermoset resin mixture is 3% phenolic thermoset
6 resin particles, 2.5% wax particles, balance molybdenum
7 particles, by weight. The proper ratio of wax, phenolic
8 thermoset resin particles, and molybdenum particles has an
9 effect on shrinkage during selective laser sintering of the
10 particle mixture to "tack" together the molybdenum particles and
11 during sintering of the desired form which vaporizes the wax and
12 phenolic thermoset resin and sinters the molybdenum particles.

13 Where mass production of simple shaped parts is desired,
14 "cold pressing" the mixture of molybdenum particles, wax
15 particles, and phenolic thermoset resin particles is the
16 preferred method of shaping a desired form.

17 A version of "rapid prototyping" is preferred where the
18 part to be manufactured is of complex or varying topography or
19 where limited numbers of parts are to be manufactured. "Rapid
20 prototyping" is a known technology to facilitate rapid product
21 development. The version of rapid prototyping as disclosed
22 herein is suitable for processing or shaping a mixture of
23 molybdenum particles, wax particles, and phenolic thermoset

1 resin particles into a desired form. This is particularly
2 advantageous for complex or varying topographies.

3 In rapid prototyping, a 3-D model produced on a computer-
4 aided design (CAD) system is mathematically divided into a large
5 number of thin layers, a few thousandths of an inch thick. The
6 different processes for rapid prototyping generally work on the
7 same basis principle, i.e., the desired part is built up in
8 small layers, about 0.003" thick to about 0.005" thick, one
9 layer at a time, starting from the bottom and working up until
10 the entire part is finished. Thus, the layers are built, and
11 simultaneously consolidated to the preceding layer, using the
12 description of that layer from the computer.

13 The preferred rapid prototyping technique is "selective
14 laser sintering" ("SLS"). SLS uses a CO₂ laser to sinter a
15 mixture of molybdenum particles, wax particles, and phenolic
16 thermoset resin particles by scanning in the horizontal plane
17 only as dictated by a current layer description in a CAD model.
18 The three dimensional solid is built up by the addition of
19 material layers.

20 The SLS machine consists of hardware and software
21 components. The hardware components include the process chamber
22 and powder engine, the controls cabinet, and the atmospheric
23 control unit. The process chamber incorporates the laser, pre-
24 heater, and the powder handling equipment. The controls cabinet

1 interprets the CAD drawing and controls and monitors the SLS
2 process. The atmospheric control unit regulates the temperature
3 and amount of N₂ flowing through the air in the chamber. It also
4 filters the air that flows through the process chamber. The
5 software components utilize the UNIX operating system and other
6 DTM Corporation proprietary applications.

7 The CAD drawing is geometrically modified to horizontally
8 divide the desired form into thin horizontal layers. These
9 layers can be adjusted in thickness, but are typically about
10 0.003" to about 0.005" in thickness. The thin layers represent
11 sintering planes to be traced by the CO₂ laser. In operation, a
12 layer of a mixture of molybdenum particles, wax particles, and
13 phenolic thermoset resin particles is spread out. When the
14 desired cross section of the layer is traced out by the CO₂
15 laser, the temperature of the mixture of molybdenum particles,
16 wax particles, and phenolic thermoset resin particles is
17 increased, and the wax and phenolic thermoset resin particles
18 fuse the molybdenum particles together. The part is then
19 lowered in the SLS machine by 0.003" to 0.005" (depending upon
20 the layer thickness), and new layers are added in a similar
21 fashion to form the solid mass. The SLS machine builds the part
22 one layer at a time by creating the bottom layer first, and then
23 adding layers until the part is finished.

1 The mixture of molybdenum particles, wax particles, and
2 phenolic thermoset resin particles was laser sintered using the
3 DTM SINTERSTATION 2500plus machine which sinters only the wax
4 and phenolic thermoset resin particles and not the molybdenum
5 particles. As described below, post processing is necessary to
6 vaporize, sublime, or "burn off" the wax and phenolic thermoset
7 resin and sinter the molybdenum particles. After this, the
8 sintered molybdenum substrate, which is porous, is infiltrated
9 with an oxygen free copper. This post-SLS processing generally
10 results in a small shrinkage due to the vaporization of the wax
11 and phenolic thermoset resin and sintering of the molybdenum
12 particles. By holding the processing variable constant, this
13 shrinkage may be compensated for in the CAD design of the part,
14 i.e., the CAD design provides for a slightly larger molybdenum,
15 wax, and phenolic shaped form, such that upon shrinkage, the
16 molybdenum-copper composite part will be the desired size.

17 The CO₂ laser used in the SLS machine is generally only
18 capable of producing enough heat to fuse low-melting thermoset
19 synthetic resin such as phenolic; as such, it is these and
20 similar low-melting point materials, such as wax, which are used
21 to mix with the molybdenum particles when the SLS process is
22 employed. Additionally, the wax and phenolic thermoset resin
23 used must suitably vaporize or sublime in the vaporization step
24 prior to sintering the molybdenum particles.

1 The desired parameters for SLS shaping of a mixture of
2 molybdenum particles, wax particles, and phenolic thermoset
3 resin particles to the desired form are as follows:

4 Layer thickness: 0.003 inches

5 Right and left feed heater temperature: 55 degrees C

6 Part heater set point: 75 degrees C

7 Laser power: 12 Watts

8 Scan spacing: 0.003 inches

9 Scan speed: 150 inches per second

10 After sintering or cold pressing has been completed, the
11 green form is placed on an aluminum oxide plate which is located
12 in a graphite crucible. Oxygen free copper is placed on top of
13 tabs, which are also formed from the molybdenum, phenolic, wax
14 mixture, that are adjacent to the green form. The amount of
15 oxygen free copper to be used is $0.72 \times$ green weight including
16 the green form and the tabs. The oxygen free copper is placed
17 on the tabs and the entire green form, tabs, and oxygen free
18 copper infiltrant material is then covered with aluminum oxide
19 in particulate form. The crucible is then placed in a furnace
20 with a process gas of 5% hydrogen, balance argon, and a process
21 pressure of 1 Torr. The green form material and the oxygen free
22 copper are subjected to a furnace cycle. The furnace cycle
23 comprises taking the green form material and the oxygen free
24 copper from room temperature (approximately 68 degrees

1 Fahrenheit) to 600 degrees Centigrade over a period of 3 hours,
2 holding at 600 degrees Centigrade for 1 hour, heating from 600
3 degrees Centigrade to 1,150 degrees Centigrade over a period of
4 2.3 hours, holding at 1,150 degrees Centigrade for 0.5 hours,
5 then reducing the temperature from 1,150 degrees Centigrade to
6 room temperature over a time period of 3 hours. During this
7 single furnace cycle, vaporization of the wax and phenolic
8 binder, sintering of the molybdenum particulate, and
9 infiltration of the sintered molybdenum particles with oxygen
10 free copper are accomplished. The vaporization step may be
11 referred to by those skilled in the art as "burn-out"; however,
12 this terminology is somewhat misleading in that it is preferred
13 that substantially no oxygen be present during the sintering
14 step. Oxygen present in the sintering step may lead to reduced
15 wetting in the copper infiltration step.

16 Vaporization and sintering produces a sintered molybdenum
17 shaped form that is about 35 volume % to about 65 volume %
18 occupied by sintered molybdenum, i.e., about 35% to about 65%
19 dense. The density may advantageously be varied, within these
20 limits, depending upon the desired application. The density or
21 porosity may be altered by varying the size or size distribution
22 of the molybdenum particles used, varying the size or size
23 distribution of either the wax or phenolic thermoset resin
24 particles used, varying the particle mixture ratio used, and/or

1 varying the manufacturing technique, etc. The density or
2 porosity determines the molybdenum-copper ratio and may be
3 optimized to meet specific objectives.

4 During the furnace operation the oxygen free copper is
5 heated above its melting point (1,083 degrees C), such that by
6 capillary action, the copper infiltrates into the open area of
7 the sintered molybdenum particles to produce the molybdenum-
8 copper composite in the desired form with an about 100% density.
9 The resulting mixture is a molybdenum-copper composite with a
10 volume fraction of molybdenum of between 35% and 65% with the
11 balance oxygen free copper.

12 Generally, the resulting average particle size diameter of
13 the composite material is 2.31 microns, the mean free path is
14 1.99 microns, and the mean center to center particle spacing is
15 4.61 microns.

16 The composite material of the present invention is unique
17 in that it offers the ability to create tools and prototype
18 parts requiring working temperatures up to 1000 degrees
19 Centigrade. The material is also advantageous because it has a
20 low coefficient of thermal expansion. The present invention is
21 also unique in that it offers properties above and beyond that
22 of the commercially available selective laser sintering material
23 systems. For example, it has a higher thermal conductivity than
24 known stainless steel-copper alloy composite materials. Since

1 an oxygen free copper (99.9% pure copper) is used in the preset
2 invention it will have better thermal conductivity than known
3 90% copper - 10% tin bronze infiltrant materials. A wide
4 variety of parts may be made from the composite material of the
5 present invention and the method of the present invention.

6 It is apparent that there has been provided in accordance
7 with the present invention a molybdenum-copper composite
8 material which fully satisfies the objects, means, and
9 advantages set forth hereinbefore. While the present invention
10 has been described in the context of specific embodiments
11 thereof, other alternatives, modifications, and variations will
12 become apparent to those skilled in the art having read the
13 foregoing description. Accordingly, it is intended to embrace
14 those alternatives, modifications, and variations as fall within
15 the broad scope of the appended claims.